Supporting Information

Regioselective Palladium-Catalyzed Formate Reduction of *N*-Heterocyclic Allylic Acetates

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General information: all catalytic reactions were carried out under nitrogen atmosphere. Commercially available compounds, including all phosphine ligands, allylamine, 1st and 2nd Grubbs' catalysts, allylpalladium chloride dimer, triethylamine and formic acid (96%, A.C.S. reagent) were used without further purification. Dichloromethane was freshly distilled from CaH_2 prior to use. Anhydrous THF was obtained by distillation over sodium/benzophenone. DMF was dried over molecular sieves (3A). ^1H and ^{13}C NMR spectra were obtained on Brüker 200 or 500 MHz spectrometers and referenced to TMS or residual CHCl_3 . Concentration of solutions was accomplished by rotary evaporation at water aspirator pressure. Analytical TLC was carried out using Merck aluminum-backed 0.2 mm silica gel 60 F254 plates. Column chromatography was conducted using Merck silica gel 60 (230-400 mesh).

Preparation of diolefin 4a. A solution of *N*-tosyl allyl amine (1.0 g, 4.73 mmol) in dry DMF (10 mL) was added to the slurry of sodium hydride (60% in mineral oil, 400 mg, 10 mmol) at 0 °C. The reaction mixture was stirred for another 30 min in an ice-water bath. Allyl bromide **3** (1.82 g, 9.47 mmol) in DMF (2 mL) was added to the reaction by syringe, and the reaction was stirred at room temperature for 16 h. The reaction mixture was terminated with water (20 mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was separated, washed with water (20 mL), sat. $\text{NaCl}_{(\text{aq})}$ (20 mL), dried over sodium sulfate, filtered and concentrated to give the crude product. The crude diene was further purified by column chromatography (SiO_2 : ethyl acetate/hexanes, 1:3; R_f 0.41) to have pure diene **4a**¹ (1.2 g, 3.71 mmol, 80%). ^1H NMR (500 MHz, CDCl_3) δ 7.67 (2 H, d, J = 8.2 Hz), 7.24 (2H, d, J = 8.1 Hz), 5.52 – 5.50 (1H, m), 5.19 (1 H, s), 5.11–5.04 (3H, m), 4.48 (2H, s), 3.78–3.75 (4H, m), 2.40 (3H, s), 2.04 (3H, s). ^{13}C NMR (125 MHz, CDCl_3) δ 170.4, 143.4, 138.5, 136.9, 132.1, 129.6, 127.1, 119.5, 117.0, 64.5, 49.6, 49.0, 21.4, 20.7. HRMS (FAB) Calcd for $[\text{M} + \text{H}]^+$ ($\text{C}_{16}\text{H}_{22}\text{NO}_4\text{S}$): 324.1270, found 324.1275.

Preparation of 4b: the procedure in preparing **4a** was followed. Starting with *N*-tosyl homoallyl amine (500 mg, 2.22 mmol), diene **4b** (220 mg, 0.71 mmol) was produced in 60% yield. R_f 0.42 (SiO_2 , ethyl acetate/hexanes, 1:3); ^1H NMR (500 MHz, CDCl_3) δ 7.67 (2H, d, J = 8.2 Hz), 7.28 (2H, d, J = 8.1 Hz), 5.65 – 5.59 (1H, m), 5.17 (2H, d, J = 23 Hz), 4.99 – 4.96 (2H, m), 4.51 (2H, s), 3.78 (2H, s), 3.15 – 3.12 (2H, m), 2.40 (3H, s), 2.20 (2H, q, J = 8.4, 7.0 Hz), 2.05 (3H, s). ^{13}C NMR (125 MHz, CDCl_3) δ 170.5, 143.4, 139.2, 136.6, 134.6, 129.7, 127.2, 117.0, 116.9, 64.5, 50.8, 47.4, 32.6, 21.5, 20.8; HRMS (FAB): Calcd for $[\text{M} + \text{H}]^+$ ($\text{C}_{17}\text{H}_{24}\text{O}_4\text{NS}$): 338.1426, found 338.1417.

Preparation of **4c**: starting with *N*-tosyl 4-pentenyl amine (50 mg, 0.21 mmol), diene **4c** (58 mg, 0.18 mmol) was produced in 86% yield. R_f 0.45 (SiO₂, ethyl acetate/hexanes, 1:3); ¹H NMR (500 MHz, CDCl₃) δ 7.66 (2H, d, J = 8.2 Hz), 7.27 (2H, d, J = 8.1 Hz), 5.71 – 5.68 (1H, m), 5.18 (1H, s), 5.14, (1H, s), 4.93 – 4.90 (2H, m), 4.50 (2H, s), 3.75 (2H, s), 3.08 – 3.05 (2H, m), 2.40 (3H, s), 2.06 (3H, s), 1.95 (2H, q, J = 7.2, 6.8 Hz), 1.56 – 1.53 (2H, m). ¹³C NMR (125 MHz, CDCl₃) δ 170.4, 143.3, 139.3, 137.3, 136.6, 129.6, 127.1, 116.7, 115.2, 64.5, 50.8, 47.7, 50.8, 47.7, 42.7, 42.6, 30.8, 28.7, 27.1, 21.4, 20.8; HRMS (FAB): Calcd for [M+H]⁺ (C₁₈H₂₆O₄NS): 352.1583, found 352.1573.

Preparation of **4d**: starting with *N*-tosyl 5-hexenyl amine (510 mg, 2.0 mmol), diene **4d** (587 mg, 1.60 mmol) was produced in 80% yield. R_f 0.56 (SiO₂, ethyl acetate/hexanes, 1:3); ¹H NMR (500 MHz, CDCl₃) δ 7.66 (2H, d, J = 8.2 Hz), 7.27 (2H, d, J = 8.0 Hz), 5.80 – 5.59 (1H, m), 5.18 (1H, s), 5.13, (1H, s), 4.95 – 4.89 (2H, m), 4.50 (2H, s), 3.75 (2H, s), 3.07 – 3.04 (2H, m), 2.39 (3H, s), 2.05 (3H, s), 1.96 (2H, m), 1.46 – 1.43 (2H, m), 1.28 – 1.25 (2H, m). ¹³C NMR (125 MHz, CDCl₃) δ 170.3, 143.1, 139.2, 138.1, 136.6, 129.5, 127.1, 116.4, 114.6, 64.4, 50.6, 47.8, 33.0, 27.2, 25.8, 21.3, 20.7; HRMS (FAB): Calcd for [M+H]⁺ (C₁₉H₂₈O₄NS): 366.1739, found 366.1745.

Preparation of **1b**: the procedure in preparing **1a** was followed. Starting with diene **4b** (400 mg, 1.18 mmol) and Grubbs catalyst, 1st generation, (10 mg, 0.01 mmol), compound **1b** (200 mg, 0.65 mmol) was produced in 60% yield. R_f 0.52 (SiO₂, ethyl acetate/hexanes, 1:1); ¹H NMR (500 MHz, CDCl₃) δ 7.64 (2H, d, J = 8.1 Hz), 7.29 (2H, d, J = 8.0 Hz), 5.77 (1H, s), 4.40 (2H, s), 3.52 (2H, s), 3.10 (2H, t, J = 5.7 Hz), 2.39 (3H, s), 2.20 (2H, s), 2.02 (3H, s). ¹³C NMR (125 MHz, CDCl₃) δ 170.6, 143.6, 133.1, 129.6, 129.4, 127.6, 124.9, 65.8, 45.2, 42.2, 24.9, 21.4, 20.8; HRMS (FAB) Calcd for [M + H]⁺ (C₁₅H₂₀O₄NS): 310.1113, found 310.1119.

Preparation of **1c**: starting with diene **4c** (550 mg, 1.56 mmol) and Grubbs catalyst 2nd generation, (27 mg, 0.031 mmol), compound **1c** (354 mg, 1.09 mmol) was produced in 70% yield. R_f 0.56 (SiO₂, ethyl acetate/hexanes, 1:1); ¹H NMR (500 MHz, CDCl₃) δ 7.64 (2H, d, J = 8.3 Hz), 7.26 (2H, d, J = 8.0 Hz), 5.81 (1H, t, J = 5.5 Hz), 4.47 (2H, s), 3.81 (2H, s), 3.36 (2H, t, J = 6.1), 2.39 (3H, s), 2.18 – 2.14 (2H, m), 2.06 (3H, s), 1.80 – 1.62 (2H, m); ¹³C NMR (125 MHz, CDCl₃) δ 170.8, 143.0, 136.2, 134.1, 132.5, 129.5, 127.0, 67.7, 49.6, 47.0, 26.3, 26.1, 21.3, 20.8; HRMS (FAB): Calcd for [M + H]⁺ (C₁₆H₂₂O₄NS): 324.1270, found 324.1267.

Preparation of **1d**: starting with diene **4d** (12 mg, 0.032 mmol) and Grubbs

catalyst 2nd generation, (5 mg, 0.0058 mmol), compound **1d** (7.5 mg, 0.022 mmol) was produced in 68% yield. R_f 0.31 (SiO₂, ethyl acetate/hexanes, 1:3); ¹H NMR (500 MHz, CDCl₃) δ 7.65 (2 H, J = 8.2 Hz), 7.27 (2 H, J = 8.1 Hz), 5.58 (1H, t, J = 8.3 Hz), 4.50 (2H, s), 3.77 (2H, s), 3.26-3.24 (2H, m), 2.38 (3H, s), 2.33 (2H, q, J = 7.9, 4.3 Hz), 2.01 (3H, s), 1.55 – 1.51 (4H, m); ¹³C NMR (125 MHz, CDCl₃) δ 170.4, 143.1, 135.9, 132.4, 130.9, 129.6, 126.9, 67.4, 47.5, 45.9, 26.5, 25.4, 24.6, 21.4, 20.8.; HRMS (FAB): Calcd for [M + H]⁺ (C₁₇H₂₄O₄NS): 338.1426, found 338.1427.

Triethyl amine (57 μ L, 0.41 mmol) and formic acid (7.7 μ L, 0.2 mmol) was added to a solution of allylpalladium chloride dimer (1.2 mg, 3.3×10^{-3} mmol) and di-*tert*-butyl 2-biphenylphosphine (3.9 mg, 0.01 mmol) in DMF (400 μ L) under the atmosphere of nitrogen. The solution was stirred for 1 minute at room temperature. Acetate **1c** (20 mg, 0.062 mmol) in DMF (400 μ L) was added to the solution of the palladium complex. After stirred at 25 °C for 25 h, the reaction mixture was diluted with CH₂Cl₂ (20 mL), extracted with water (3 mL $\times$ 2), sat. NaCl_(aq) (5 mL), and dried over Na₂SO₄, filtered, concentrated and purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:9; R_f 0.45) to have compound **5a** (10.5 mg, 0.42 mmol, 68%). ¹H NMR (500 MHz, CDCl₃) δ 7.69 (2H, d, J = 8.1 Hz), 7.31 (2H, d, J = 7.9 Hz), 4.89 (2H, dt, J = 9.3, 1.96 Hz), 3.75 (1H, s), 3.26 (2H, t, J = 7.0 Hz), 2.45 (2H, t, J = 6.9 Hz), 2.45 (3H, s). ¹³C NMR (125 MHz, CDCl₃) δ 144.0, 143.6, 132.6, 129.6, 127.8, 107.3, 51.8, 48.0, 31.7, 21.5.

Triethyl amine (52 μ L, 0.37 mmol) and formic acid (7 μ L, 0.18 mmol) was added to a solution of allylpalladium chloride dimer (1.2 mg, 3.3×10^{-3} mmol) and di-*tert*-butyl 2-biphenylphosphine (3.7 mg, 0.010 mmol) in DMF (400 μ L) under the atmosphere of nitrogen. The solution was stirred for 1 minute and cooled to 0 °C. Acetate **1c** (20 mg, 0.062 mmol) in DMF (400 μ L) was added to the solution of the palladium complex. After stirred at 0 °C for 14 h, the reaction mixture was diluted with CH₂Cl₂ (20 mL), extracted with water (3 mL $\times$ 2), sat. NaCl_(aq) (5 mL), and dried over Na₂SO₄, filtered, concentrated and purified by column chromatography

(SiO₂: ethyl acetate/hexanes, 1:3; *R_f* 0.66) to have pure compound **5c** (13.3 mg, 0.05 mmol, 81%). ¹H NMR (500 MHz, CDCl₃) δ 7.66 (2H, d, *J* = 8.1 Hz), 7.27 (2H, d, *J* = 8.0 Hz), 4.85 (1H, s), 4.79 (1H, s), 3.85 (2 H, s), 3.15 (2H, t, *J* = 5.2 Hz), 2.40 (3H, s), 2.26 (2H, t, *J* = 5.6 Hz), 1.70–1.68 (2H, m), 1.56–1.54 (2H, m). ¹³C NMR (125 MHz, CDCl₃) δ 147.0, 142.9, 136.5, 129.6, 126.9, 113.1, 54.6, 48.0, 34.0, 30.5, 29.3, 21.4.; HRMS (FAB) Calcd for [M + H]⁺ (C₁₄H₂₀O₂NS) : 266.1215, found 266.1216.

Triethyl amine (50 μL, 0.35 mmol) and formic acid (7 μL, 0.18 mmol) was added to a solution of allylpalladium chloride dimer (1.1 mg, 3.3×10⁻³ mmol) and di-*tert*-butyl 2-(2'-methylbiphenyl)phosphine (3.7 mg, 0.010 mmol) in DMF (200 μL) under the atmosphere of nitrogen. The solution was stirred for 1 minute and cooled to 0 °C. Acetate **1d** (20 mg, 0.060 mmol) in DMF (400 μL) was added to the solution of the palladium complex. After stirred at 0 °C for 14 h, the reaction mixture was diluted with CH₂Cl₂ (20 mL), extracted with water (3 mL × 2), sat. NaCl_(aq) (5 mL), and dried over Na₂SO₄, filtered, concentrated and purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:9; *R_f* 0.43) to have pure compound **5d** (13.2 mg, 0.047 mmol, 80%). ¹H NMR (500 MHz, CDCl₃) δ 7.64 (2H, d, *J* = 8.2 Hz), 7.28 (2H, d, *J* = 8.0 Hz), 4.86 (1H, s), 4.84 (1H, s), 3.68 (2 H, s), 3.04 (2H, m), 2.40 (3H, s), 2.30–2.28 (2H, m), 1.69–1.67 (2H, m), 1.67–1.64 (4H, m). ¹³C NMR (125 MHz, CDCl₃) δ 147.5, 143.0, 135.6, 129.6, 127.1, 114.2, 55.5, 48.1, 34.0, 33.7, 30.0, 27.9, 24.7, 21.4.; HRMS (FAB) Calcd for [M + H]⁺ (C₁₅H₂₂O₂NS) : 280.1371, found 280.1376.

Independent synthesis of endo cyclic olefins **6b-d**:

A solution of *N*-tosyl homoallyl amine (200 mg, 0.89 mmol) in dry DMF (2 mL) was added to the slurry of sodium hydride (60% in mineral oil, 71mg, 1.77 mmol) at 0 °C. The reaction mixture was stirred for another 30 min in an ice-water bath. 3-Chloro-2-methylpropene (175 μL, 1.77 mmol) was added to the reaction by syringe, then the ice-water bath was removed and the reaction was heated to reflux for 17 h.

The reaction was quenched with water (5 mL), diluted with CH₂Cl₂ (20 mL). The organic layer was separated, washed with water (5 mL), sat. NaCl_(aq) (10 mL), dried over sodium sulfate, filtered and concentrated to give the crude product. The crude diene was further purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:3; *R_f* 0.65) to have pure diene **8** (235 mg, 0.84 mmol, 95%). ¹H NMR (500 MHz, CDCl₃) δ 7.67 (2H, d, *J* = 8.1 Hz), 7.29 (2H, d, *J* = 8.0 Hz), 5.65 – 5.58 (1H, m), 4.98 – 4.94 (2H, m), 4.87 (2H, d, *J* = 9.4 Hz), 3.67 (2H, s), 3.12 – 3.09 (2H, m), 2.39 (3H, s), 2.20 (2H, q, *J* = 8.1, 7.1), 1.62 (3H, s); ¹³C NMR (125 MHz, CDCl₃) δ 143.1, 140.7, 137.0, 134.8, 129.6, 127.1, 116.8, 114.4, 54.6, 47.2, 32.6, 21.4, 19.8.

Diene **8** (50 mg, 0.18 mmol) and Grubbs catalyst 1st generation (3 mg, 0.004 mmol) in CH₂Cl₂ (2 mL) was heated to reflux for 2h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:1; *R_f* 0.61) to have the *endo* olefin **6b** (45 mg, 0.18 mmol, 89%). ¹H NMR (500 MHz, CDCl₃) δ 7.65 (2H, d, *J* = 8.1 Hz), 7.29 (2H, d, *J* = 8.1 Hz), 5.40 (1 H, s), 3.38 (2 H, s), 3.07 (2H, t, *J* = 5.7 Hz), 2.40 (3 H, s), 2.13 (2H, s), 1.60 (3H, 3). ¹³C NMR (125 MHz, CDCl₃) δ 143.4, 133.2, 129.8, 129.6, 127.6, 119.3, 48.2, 42.5, 25.1, 21.5, 20.5. HRMS (FAB) Calcd for [M + H]⁺ (C₁₃H₁₈O₂NS): 252.1058, found 252.1057.

A solution of *N*-tosyl 4-pentenyl amine (30 mg, 0.12 mmol) in dry DMF (1 mL) was added to the slurry of sodium hydride (60% in mineral oil, 10 mg, 0.025 mmol) at 0 °C. The reaction mixture was stirred for another 30 min in an ice-water bath. 3-Chloro-2-methylpropene (50 μL, 0.50 mmol) was added to the reaction by syringe, then the ice-water bath was removed and the reaction was heated to reflux for 16 h. The reaction was quenched with water (5 mL), diluted with CH₂Cl₂ (20 mL). The organic layer was separated, washed with water (5 mL), sat. NaCl_(aq) (10 mL), dried over sodium sulfate, filtered and concentrated to give the crude product. The crude diene was further purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:6; *R_f* 0.51) to have pure diene **9** (29 mg, 0.10 mmol, 88%). ¹H NMR (500 MHz, CDCl₃) δ 7.66 (2H, d, *J* = 8.2 Hz), 7.27 (2H, d, *J* = 8.1 Hz), 5.72 – 5.67 (1H, m), 4.97 – 4.91 (2H, m), 4.87 (1H, s), 4.85 (1H, s), 3.65 (2H, s), 3.04 (2H, t, *J* = 7.9 Hz), 2.40 (3H, s), 1.96 (2H, q, *J* = 7.2, 6.8), 1.69 (3H, s), 1.54 (2H, m). ¹³C NMR (125 MHz, CDCl₃) δ 143.0, 140.9, 137.4, 137.0, 129.5, 127.1, 115.0, 114.2, 54.6, 47.5, 30.8, 29.6, 27.1, 21.4, 19.7.; HRMS (FAB) Calcd for [M + H]⁺ (C₁₆H₂₄O₂NS): 294.1528, found 294.1527.

Diene **9** (29 mg, 0.10 mmol) and Grubbs catalyst 2nd generation (2 mg, 0.0023 mmol) in CH₂Cl₂ (1 mL) was heated to reflux for 14 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:6 ; *R_f* 0.50) to have the *endo* olefin **6c** (19.5 mg, 0.073 mmol, 75%). ¹H NMR (500 MHz, CDCl₃) δ 7.64 (2H, d, *J* = 8.2 Hz), 7.26 (2H, d, *J* = 8.0 Hz), 5.46–5.44 (1 H, m), 3.70 (2 H, s), 3.34 (2H, t, *J* = 6.2 Hz), 2.39 (3 H, s), 2.07 (2H, q, *J* = 5.4, 4.6 Hz), 1.74 (2H, m), 1.68 (3H, s). ¹³C NMR (125 MHz, CDCl₃) δ 142.9, 136.5, 134.6, 129.4, 127.0, 126.6, 50.7, 49.6, 27.0, 25.7, 23.1, 21.4; HRMS (FAB) Calcd for [M + H]⁺ (C₁₄H₂₀O₂NS) : 266.1215, found 266.1202.

A solution of *N*-tosyl 5-hexenyl amine (30 mg, 0.12 mmol) in dry DMF (1 mL) was added to the slurry of sodium hydride (60% in mineral oil, 16 mg, 0.39 mmol) at 0 °C. The reaction mixture was stirred for another 30 min in an ice-water bath. 3-Chloro-2-methylpropene (77 μL, 0.78 mmol) was added to the reaction by syringe, then the ice-water bath was removed and the reaction was heated to reflux for 16 h. The reaction was quenched with water (5 mL), diluted with CH₂Cl₂ (20 mL). The organic layer was separated, washed with water (5 mL), sat. NaCl_(aq) (10 mL), dried over sodium sulfate, filtered and concentrated to give the crude product. The crude diene was further purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:6; *R_f* 0.51) to have pure diene **10** (30 mg, 0.11 mmol, 96%). ¹H NMR (500 MHz, CDCl₃) δ 7.66 (2H, d, *J* = 8.2 Hz), 7.26 (2H, d, *J* = 8.1 Hz), 5.72 – 5.67 (1H, m), 4.94 – 4.88 (2H, m), 4.86 (1H, s), 4.84 (1H, s), 3.65 (2H, s), 3.03 (2H, t, *J* = 7.8 Hz), 2.39 (3H, s), 1.96 (2H, q, *J* = 7.3, 7.0), 1.68 (3H, s), 1.44 (2H, m), 1.26 (2H, m); ¹³C NMR (125 MHz, CDCl₃) δ 143.0, 140.9, 138.3, 137.1, 129.5, 127.1, 114.6, 114.2, 54.5, 47.7, 33.1, 27.3, 26.0, 21.4, 19.7.; HRMS (FAB) Calcd for [M+H]⁺ (C₁₇H₂₆O₂NS) : 308.1684, found 308.1679.

Diene **10** (12 mg, 0.039 mmol) and Grubbs catalyst 2nd generation (2 mg, 0.0023 mmol) in CH₂Cl₂ (7 mL) was heated to reflux for 14 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂: ethyl acetate/hexanes, 1:9 ; *R_f* 0.43) to have the *endo* olefin **6d** (7.7 mg, 0.027 mmol, 70%). ¹H NMR (500 MHz, CDCl₃) δ 7.65 (2H, d, *J* = 8.2 Hz), 7.27 (2H, d, *J* = 8.1 Hz), 5.52–5.49 (1 H, m), 3.65 (2 H, s), 3.26 (2H, dd, *J* = 5.4, 4.8 Hz), 2.40 (3 H, s), 2.26 (2H, q, *J* = 7.7, 4.9 Hz), 1.64 (3H, s), 1.53–1.46 (4H, m). ¹³C NMR (125 MHz, CDCl₃) δ 142.9, 136.3, 131.7, 129.6, 127.0, 49.1, 47.6, 27.2, 25.4,

24.8, 22.3, 21.4.; HRMS (FAB) Calcd for [M + H]⁺ (C₁₅H₂₂O₂NS): 280.1371, found 280.1359.

Reference:

(1) Oppolzer, W.; Swenson, R. E.; Gaudin, J. M. . *Tetrahedron Lett.* **1988**, 29, 5529.

ppm

4b

5b

5d

5d

ppm

6a

ppm

6b

143.414
133.164
129.823
129.556
127.629
119.345

77.248
76.994
76.740

48.177
42.468

25.070
21.462
20.538

ppm

180

160

140

120

100

S37

80

60

40

20

6d

6d